

Volume term of work of critical nucleus formation in terms of chemical potential difference relative to equilibrium one

Atsushi Mori¹

*Institute of Technology and Science, The University of Tokushima, 2-1
Minamijosanjima, Tokushima 770-8506, Japan*

Abstract

The work of formation of a critical nucleus is sometimes written as $W = n\Delta\mu + \gamma A$. The first term $W_{vol} = n\Delta\mu$ is called the volume term and the second term γA the surface term with γ being the interfacial tension and A the area of the nucleus. Nishioka and Kusaka [J. Chem. Phys. **96** (1992) 5370] derived $W_{vol} = n\Delta\mu$ with $n = V_\beta/v_\beta$ and $\Delta\mu = \mu_\beta(T, p_\alpha) - \mu_\alpha(T, p_\alpha)$ by rewriting $W_{vol} = -(p_\beta - p_\alpha)V_\beta$ by integrating the isothermal Gibbs-Duhem relation for an incompressible β phase, where α and β represent the parent and nucleating phases, V_β is the volume of the nucleus, v_β , which is constant, the molecular volume of the β phase, μ , T , and p denote the chemical potential, the temperature, and the pressure, respectively. We note here that $\Delta\mu = \mu_\beta(T, p_\alpha) - \mu_\alpha(T, p_\alpha)$ is, in general, not a directly measurable quantity. In this paper, we have rewritten $W_{vol} = -(p_\beta - p_\alpha)V_\beta$ in terms of $\mu_{re} - \mu_{eq}$, where μ_{re} and μ_{eq} are the chemical potential of the reservoir (equaling that of the real system, common to the α and β phases) and that at equilibrium. Here, the quantity $\mu_{re} - \mu_{eq}$ is the directly measurable supersaturation. The obtained form is similar to but slightly different from $W_{vol} = n\Delta\mu$.

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¹Corresponding author: E-mail atsushimori@tokushima-u.ac.jp, Tel +81-88-656-9417, Fax +81-88-656-9435

1. Introduction

To calculate the reversible work of formation of a critical nucleus is one of the purposes of the theory of nucleation, because one can predict the steady state nucleation rate $J_s = J_0 \exp(-W^*/k_B T)$ through the work of formation of the critical nucleus W , where $k_B T$ is the temperature multiplied by Boltzmann's constant. Here, $W^* \equiv W(R^*)$ is the height of the nucleation barrier with R^* being the radius of the critical nucleus. We can refer a theory not including molecular level quantities to as a classical nucleation theory. We often encounter the following formula [Eq. (1)] or equivalent one in the classical nucleation theory:

$$W = n\Delta\mu + \gamma A, \quad (1)$$

with γ being the interfacial tension, $A \equiv 4\pi R^2$ the area of the interface (rigorously speaking, R is the radius of the surface of tension) in textbooks such as [1, 2, 3, 4, 5, 6] as well as research papers such as [7, 8, 9, 10, 11, 12, 13]. Nishioka and Kusaka [14] called this formula “a commonly used formula.” In this formula, one regards $\Delta\mu$ the chemical potential difference between the parent phase (the α phase) and the nucleating phase (the β phase), i.e., $\Delta\mu \equiv \mu_\beta - \mu_\alpha (< 0)$ [in the field of crystal growth, one sometimes defines the supersaturation as $\Delta\mu \equiv \mu_\alpha - \mu_\beta (> 0)$ and the negative sign arises as $-n\Delta\mu$]. We note here that the term “supersaturation” is sometimes used to express the such thermodynamic driving force, apart from the literal meaning. In this paper, we will adopt this terminology. One can understand n as the numbers of molecules undergone the phase transition from the α phase to the β phase. Apart from its implication, meaning of $\Delta\mu$ in this expression is immediately ambiguous; for the critical nucleus, the chemical potential of the β phase is equal to that of the α phase. In this paper, we will give correct formulas for W in terms of the chemical potential difference relative to equilibrium one.

The exactly correct form for W given by Gibbs [15] is

$$W = -(p_\beta - p_\alpha)V_\beta + \gamma A, \quad (2)$$

where p denotes the pressure and $V_\beta \equiv 4\pi R^3/3$ is the volume of the nucleus. Rigorously speaking, p_β is the pressure of the hypothetical cluster defined such as possessing the bulk property and filling the inside of the surface of tension, and thus V_β the volume inside the surface of tension. A transparent

explanation for the volume term $W_{vol} = -(p_\beta - p_\alpha)V_\beta$ can be given through a grand potential formalism — the grand potential is defined as $\Omega = -pV$; the grand potential formalism for interfaces was given in, for example, a textbook by Landau and Lifshitz [16] and exactness of $W_{vol} = -(p_\beta - p_\alpha)V_\beta$ is shown by a textbook by Vehkamäki [17] (see also [18]). The author wish to introduce a heuristic paper [19] for readers' convenience. That is, one can readily understand the form of W_{vol} on the basis of the fact that the reversible work of formation of the critical nucleus is the grand potential difference. In the following sense, Eq. (2) is entirely exact. We divide the process of nucleus formation into two. One is the formation of a hypothetical cluster of radius R , within which the bulk β phase fulfills. The other is the formation of interfacial structure on the mathematical boundary of radius R . The former is given by the first term in Eq. (2) and the latter is expressed by the second term. The problem of classical theories is that the interfacial tension γ is treated as constant (in particular, in a capillary approximation γ for the flat interface is employed), whereas the curvature dependence is unnecessarily negligible [20, 21, 22, 23, 24, 25, 26, 27].

In Sec. 2 we will give the derivation of $W_{vol} = n[\mu_\beta(T, p_\alpha) - \mu_\alpha(T, p_\alpha)]$ due to Nishioka and Kusaka [14]. Here, we will give a brief review on this form. To express the pressures in terms of the chemical potentials using the Gibbs-Duhem relation was seen in Oxtoby and Kashchiev's paper on the nucleation theorem [28]. In their paper, however, W_{vol} was not calculated. Laaksonen *et al.* [29] pointed out that W_{vol} could be calculated by extending the Oxtoby and Kashchiev's line. This is completely the same as Nishioka and Kusaka's [14]. Also, the same procedure was followed by Debenedetti and Reiss [30]. In order to avoid defocusing of the point of the present paper, we will not give a general review on the nucleation theorem.

Differentiating Eq. (2) with respect to R and equating zero and then solving for R , we have formula for the size of the critical nucleus as

$$R^* = \frac{2\gamma}{p_\beta - p_\alpha}. \quad (3)$$

By substituting Eq. (3) for R in Eq. (2) the hight of the nucleation barrier is obtained as

$$W^* = \frac{1}{2}(p_\beta - p_\alpha)V_\beta^* = \frac{1}{3}\gamma A^* = \frac{16\pi\gamma^3}{3(p_\beta - p_\alpha)^2}, \quad (4)$$

with $V_\beta^* \equiv 4\pi(R^*)^3/3$ and $A^* \equiv 4\pi(R^*)^2$. Corresponding to Eq. (1), one has

$$W^* = \frac{16\pi v^2 \gamma^3}{3(\Delta\mu)^2}, \quad (5)$$

instead of the last expression of Eq. (4). Here, v represent “the molecular volume”; that is, n (or n^*) is expressed as V_β/v (or V_β^*/v). We note here that the definition of v is immediately ambiguous; whose phase is not specified, or v may be common to the α and β phases. Also, as mentioned above, the definition of $\Delta\mu$ immediately unclear. For a rarefied α phase, one uses very often

$$\Delta\mu = k_B T \ln S, \quad (6)$$

where S is the supersaturation ratio p_{re}/p_{eq} with p_{re} being the pressure of the reservoir, which equals p_α , and p_{eq} the equilibrium pressure. In other words, $\Delta\mu$ is defined as

$$\Delta\mu = \mu_\alpha(T, p_{re}) - \mu_\alpha(T, p_{eq}), \quad (7)$$

where T is the temperature, which is assumed to be uniform throughout the system. Hereafter, T will be omitted for brevity. As shall be shown below, this definition is, however, incorrect. Nevertheless, expression W^* in terms of this $\Delta\mu$ is strongly desired because this quantity is directly measurable. Indeed, Eq. (7) is widely used such as in [31, 32, 33, 34, 35, 36, 37].

2. Derivation of commonly used formula

Nishioka and Kusaka [14] found out that in case that the β phase is incompressible, the volume term $W_{vol} = -(p_\beta - p_\alpha)V_\beta$ can be rewritten in the form $n(\mu_\beta - \mu_\alpha)$. That is, they integrated

$$\left(\frac{\partial\mu}{\partial p}\right)_T = v, \quad (8)$$

which is nothing other than Gibbs-Duhem relation for the isothermal case, for the β phase. Unfortunately, they concluded incorrectly that the form (1) was valid only for the case of the incompressible β phase such as the nucleation of an incompressible liquid phase in a vapor phase. For example, this condition is, in a mathematical form, valid for a bubble nucleation in an incompressible liquid phase. In this paper, however, we limit ourselves to

the incompressible β phase to avoid the confusion in argument. Note that the form of Eq. (1) cannot be derived in general — we can derive in some approximations.

For the case of the incompressible β phase, W_{vol} is given by [14]

$$W_{vol} = \frac{V_\beta}{v_\beta} [\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)]. \quad (9)$$

To reach to this expression we have used the fact that the chemical potential of the nucleation phase $\mu_\beta(p_\beta)$ is equal to that of the parent phase $\mu_\alpha(p_\alpha)$, i.e.,

$$\mu_\beta(p_\beta) = \mu_\alpha(p_\alpha), \quad (10)$$

(that is, the chemical potential is uniform throughout the system) as indicated by a horizontal dashed lines in Fig. 1. The vertical solid lines in Fig. 1 depicts $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ [Eq. (9)]. Figure 1 (a) is for a normal case such as a liquid droplet in a vapor phase. On the other hand, Fig. 1 (b) is for an abnormal case such as formation a nucleus of less denser, incompressible β phase in a denser α phase. In both cases, $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ does not coincide to the supersaturation, which is the chemical potential difference relative to the chemical potential at the α - β phase equilibrium (sometimes with a negative sign as note in Sec. 1).

3. Volume term in general

In these ways, one knows two cases where the form of eq. (1) is valid. Let us develop a general consideration; we consider the case that v in eq. (8) is a function of p according to the mean value theorem. Following Nishioka and Kusaka [14] we integrate the Gibbs-Duhem relation of the form of eq. (8) from p_1 to p_2 .

$$\mu(p_2) - \mu(p_1) = v(\tilde{p})(p_2 - p_1), \quad (11)$$

where \tilde{p} is a certain value lying in the interval (p_2, p_1) . Let us define p_{eq} as the equilibrium pressure of the α - β phase equilibrium (the saturation pressure of the α phase with respect to the β phase), which is the solution to

$$\mu_\beta(p) = \mu_\alpha(p). \quad (12)$$

For latter convenience, let us define an abbreviation μ_{eq} for $\mu_\beta(p_{eq}) = \mu_\alpha(p_{eq})$. Also for latter convenience, we define $\mu_{re} \equiv \mu_\beta(p_\beta) = \mu_\alpha(p_\alpha)$, which is the

chemical potential of the reservoir in μVT ensemble. Applying eq. (11) for the β and α phase, we have $\mu_\beta(p_\beta) - \mu_\beta(p_{eq}) = v_\beta(p_{eq} + \theta_\beta(p_\beta - p_{eq}))(p_\beta - p_{eq})$ and $\mu_\alpha(p_\alpha) - \mu_\alpha(p_{eq}) = v_\alpha(p_{eq} + \theta_\alpha(p_\alpha - p_{eq}))(p_\alpha - p_{eq})$ with θ_β and θ_α being certain values laying in an interval (0,1), i.e.,

$$\mu_{re} - \mu_{eq} = v_\beta(\tilde{p}_\beta)(p_\beta - p_{eq}), \quad (13)$$

$$\mu_{re} - \mu_{eq} = v_\alpha(\tilde{p}_\alpha)(p_\alpha - p_{eq}), \quad (14)$$

where v_β and v_α are molecular volumes of respective phase, \tilde{p}_β and \tilde{p}_α certain values respectively lying in intervals (p_{eq}, p_β) and (p_{eq}, p_α) for cases of $p_\beta > p_\alpha > p_{eq}$ as shown in Fig. 2 (a) [for cases of $p_\alpha < p_\beta < p_{eq}$ as shown in Fig. 2 (b) the intervals are replaced with (p_β, p_{eq}) and (p_α, p_{eq}) , respectively]. By dividing Eq. (13) by $v_\beta(\tilde{p}_\beta)$ and Eq. (14) by $v_\alpha(\tilde{p}_\alpha)$ and subtracting the latter from the former, we eliminate p_{eq} to have

$$\left[\frac{1}{v_\beta(\tilde{p}_\beta)} - \frac{1}{v_\alpha(\tilde{p}_\alpha)} \right] (\mu_{re} - \mu_{eq}) = p_\beta - p_\alpha. \quad (15)$$

We can rewrite the first term in Eq. (2) by substituting $p_\beta - p_\alpha$ by Eq. (15).

$$\begin{aligned} W_{vol} &= - \left[\frac{1}{v_\beta(\tilde{p}_\beta)} - \frac{1}{v_\alpha(\tilde{p}_\alpha)} \right] (\mu_{re} - \mu_{eq}) V_\beta \\ &= -(n_\beta - n_\alpha)(\mu_{re} - \mu_{eq}), \end{aligned} \quad (16)$$

where $n_\beta \equiv V_\beta/v_\beta(\tilde{p}_\beta)$ and $n_\alpha \equiv V_\beta/v_\alpha(\tilde{p}_\alpha)$. This form is slightly different from the first term in Eq. (1). In a case that the α phase is a rarefied vapor phase, the quantity n_α tends to vanish and the form of the first term in eq. (1) is obtained. This case can be included in the case of Fig. 1 (a) (nucleation of an incompressible liquid droplet in an infinitely rarefied vapor). In this case the curve of μ_α tends to a vertical line. In this limiting case the horizontal location of the intersection of horizontal dashed line with the μ_α curve locates on the intersection of two μ curves; that is, $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ in eq. (9) tends to coincide to $\mu_{re} - \mu_{eq}$. Here, we note that $-(\mu_{re} - \mu_{eq})$ is the true supersaturation for the case of $p_\beta > p_\alpha > p_{eq}$ [Fig. 2 (a)] and the true undersaturation for the case of $p_\beta < p_\alpha < p_{eq}$ [Fig. 2 (b)]. In this way, we have successfully express the work term in terms of the supersaturation and revealed under what case the commonly used formula holds.

We have obtained a form of Eq. (1) with $\Delta\mu = \mu_{re} - \mu_{eq}$. The result of Eq. (16) includes an issue concerning physicochemical problems, although

it is of a mathematically beautiful form; in definitions $n_\beta \equiv V_\beta/v_\beta(\tilde{p}_\beta)$ and $n_\alpha \equiv V_\beta/v_\alpha(\tilde{p}_\alpha)$, the denominators $v_\beta(\tilde{p}_\beta)$ and $v_\alpha(\tilde{p}_\alpha)$ are not fixed constant values. We will give a prompt solution here. Assuming a smallness of $\mu_{re} - \mu_{eq}$ [rigorously speaking the smallness should be described in terms of a dimensionless quantity — that is, the present statement reads $|(\mu_{re} - \mu_{eq})/\mu_{eq}| \ll 1$ or $|\mu_{re} - \mu_{eq}|/k_B T \ll 1$], let us make an second-order expansion instead of Eqs. (13) and (14). Instead of Eq. (8), it is more convenient to start with

$$\left(\frac{\partial p}{\partial \mu}\right)_T = \rho, \quad (17)$$

with $\rho = 1/v$ being the number density. The second-order expansions are

$$\begin{aligned} p_\beta - p_{eq} &= \rho_\beta(p_{eq})(\mu_{re} - \mu_{eq}) + \frac{1}{2}\rho_\beta^2(p_{eq})\kappa_\beta(p_{eq})(\mu_{re} - \mu_{eq})^2 \\ &\quad + O((\mu_{re} - \mu_{eq})^3), \end{aligned} \quad (18)$$

$$\begin{aligned} p_\alpha - p_{eq} &= \rho_\alpha(p_{eq})(\mu_{re} - \mu_{eq}) + \frac{1}{2}\rho_\alpha^2(p_{eq})\kappa_\alpha(p_{eq})(\mu_{re} - \mu_{eq})^2 \\ &\quad + O((\mu_{re} - \mu_{eq})^3), \end{aligned} \quad (19)$$

where κ denotes the isothermal compressibility. Subtraction Eq. (19) from Eq. (18), we have

$$\begin{aligned} p_\beta - p_\alpha &= [\rho_\beta(p_{eq}) - \rho_\alpha(p_{eq})](\mu_{re} - \mu_{eq}) \\ &\quad + \frac{1}{2}[\rho_\beta^2(p_{eq})\kappa_\beta(p_{eq}) - \rho_\alpha^2(p_{eq})\kappa_\alpha(p_{eq})](\mu_{re} - \mu_{eq})^2 \\ &\quad + O((\mu_{re} - \mu_{eq})^3). \end{aligned} \quad (20)$$

Neglecting the second and higher order terms in Eq. (20) and inserting in the first term of Eq. (2), we have the form of Eq. (16) with fixed n_β and n_α as an approximation. Taking into account the second term, we can improve the approximation.

Coincidence between the present result and the commonly used formula with Eq. (7) can be understood as follows. For nucleations of incompressible β phase in a rarefied gas $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ can be rewritten as

$$\begin{aligned} \mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha) &= [\mu_\beta(p_\alpha) - \mu_{eq}] - [\mu_\alpha(p_\alpha) - \mu_{eq}] \\ &= [\mu_\beta(p_\alpha) - \mu_\beta(p_{eq})] - [\mu_\alpha(p_\alpha) - \mu_\alpha(p_{eq})] \\ &= v_\beta(p_\alpha - p_{eq}) - k_B T \ln \frac{p_\alpha}{p_{eq}}. \end{aligned} \quad (21)$$

The last term can be expanded in $p_\alpha - p_{eq}$ as

$$\begin{aligned}
k_B T \ln \frac{p_\alpha}{p_{eq}} &= k_B T \ln \left[1 + \frac{p_\alpha - p_{eq}}{p_{eq}} \right] \\
&\cong k_B T \frac{p_\alpha - p_{eq}}{p_{eq}} \\
&= v_\alpha(p_{eq})(p_\alpha - p_{eq}).
\end{aligned} \tag{22}$$

To reach to the last line, the equation of state for the ideal gas has been used. Because the α phase is a rarefied gas, the inequality $v_\alpha \gg v_\beta$ holds and then we find that the first term in Eq. (21) can be neglected.

4. Discussion

In 1984, Wilemski [38] divided the number of molecule of species i included in a nucleus for the binary system as

$$n_i = n_i^b + n_i^s, \tag{23}$$

with the superscripts b and s denoting bulk and surface and wrote down the condition of the critical nucleus as

$$\begin{aligned}
0 &= (\Delta\mu + \gamma(\partial A/n_j)_{n_i})(dn_j)_{n_i} \\
&\quad + n_1^b d\mu_1^l + n_2^b d\mu_2^l \\
&\quad + n_1^s d\mu_1^l + n_2^s d\mu_2^l + A d\gamma \quad (\text{const. } T, P).
\end{aligned} \tag{24}$$

In 1999, Laaksonen *et al.* [29] revealed the work of formation of the nucleus underlying Eq. (24) as

$$\Delta G = \sum_i (\mu_{li}(P_v) - \mu_{vi}(P_v))g_i + A\gamma, \tag{25}$$

with $g_i \equiv n_{li} - n_{vi} + n_{si}$, where the subscripts l and v denote the liquid and vapor phases (in Wilemski's paper, the starting equation is $\Delta G = n_1 \Delta\mu_1 + n_2 \Delta\mu_2 + A\gamma$). The so-called surface excess number of molecules, n_s , is identical to the superficial number of molecules in the Gibbs interfacial thermodynamics [15] and we find that n_s is proportional to A .

As mentioned in Sec. 1, in the Gibbs interfacial thermodynamics the work of nucleus formation is divided into the formation of the hypothetical cluster

and that of the interfacial structure. A quantity proportional to a superficial quantity is categorized as the latter. In this respect, in Eq. (25) the volume term is regarded as

$$W_{vol} = \sum_i (\mu_{li}(P_v) - \mu_{vi}(P_v))(n_{li} - n_{vi}) \quad (26)$$

While the factors regarded as $\Delta\mu$ are different with each other in Eqs. (16) and (26), the coefficients to “ $\Delta\mu$ ” coincide with each other. The difference is that in Eq. (25) the quantity $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ appears, not the quantity $\mu_{re} - \mu_{eq}$.

5. Concluding remarks

We have successfully rewritten the volume term of the work of formation of a critical nucleus in terms of the supersaturation. The result is similar to the form of $W_{vol} = n\Delta\mu$ but slightly different; n in this form has been replaced with $n_\beta - n_\alpha$. The form $W_{vol} = n\Delta\mu$ with $\Delta\mu$ being the supersaturation (the chemical potential difference relative to equilibrium) is recovered in a limiting case that the parent phase is a rarefied gas. This is a finding that requires a concerning note in textbooks — as mentioned in Sec. 1, some textbooks lead readers to understanding that $W_{vol} = n\Delta\mu$ is exact, and in some literatures this form is valid only for an incompressible nucleating phase.

We wish to postpone comparisons with experimental studies after formulation in a form of the nucleation theorem. That is, W^* should be plotted against experimentally determined $\Delta\mu$ ’s to evaluate the differential coefficient. In relation with experiments, a crucial comment arises: the mathematical formula itself (without expansion made in the latter part of Sec. 3) makes a sense — if one forcibly write the work of formation of a critical nucleus in the form like Eq. (1), then uncertainties necessarily accompany in interpreting the experimental results.

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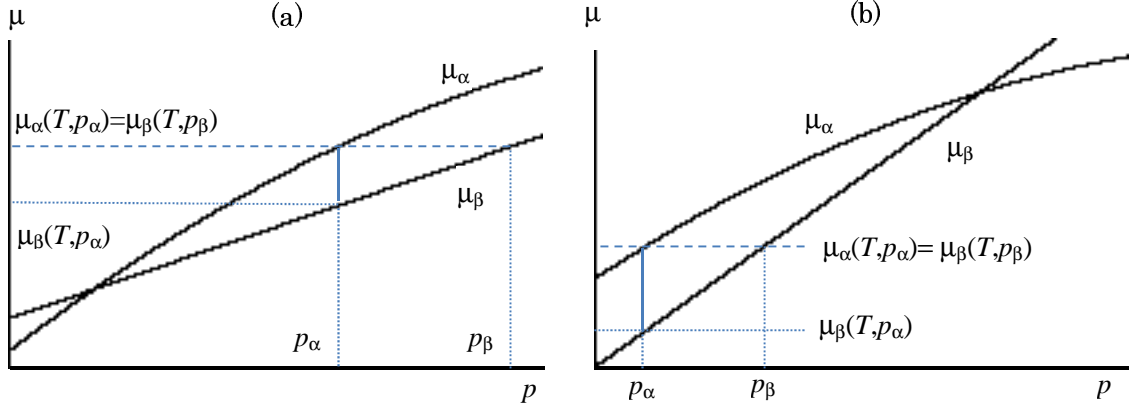


Figure 1: μ - p relation for cases of incompressible β phases; (a) a normal case that the β phase is denser than the α phase and (b) an abnormal case that the α phase is denser than the β phase. The horizontal dashed lines indicate the chemical potential, which is common to the nucleus and the parent phase. The vertical solid lines depict $\mu_\beta(p_\alpha) - \mu_\alpha(p_\alpha)$ [eq. (9)].

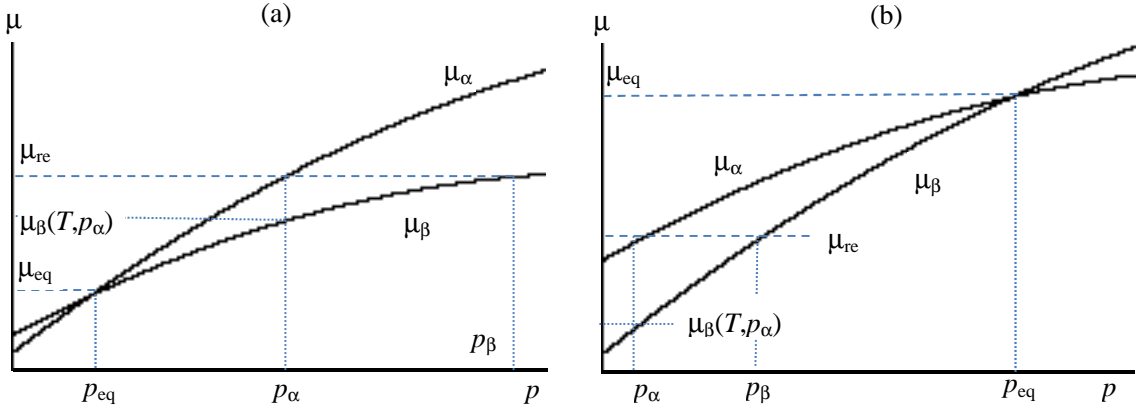


Figure 2: Location of μ_{eq} , p_β , p_α , and p_{eq} is illustrated (note that the reservoir pressure p_{re} coincides to p_α); (a) a case of condensation, i.e., the β phase is denser than the α phase, and (b) a case of bubble nucleation, i.e., the α phase is denser than the β phase. In case (a), $p_\beta > p_\alpha > p_{eq}$ holds. On the other hand, in case (b), $p_\alpha < p_\beta < p_{eq}$ holds.